

CALORIMETRY, ACTIVITY AND MICRO-FTIR ANALYSIS OF CO CHEMISORPTION,
TITRATION AND OXIDATION ON SUPPORTED Pt

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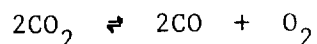
SUMMARY

The value of in-situ analysis on CO chemisorption, titration and oxidation over supported Pt catalysts using calorimetry, catalytic and micro-FTIR methods is illustrated using silica- and titania-supported samples.

INTRODUCTION

Catalysis of CO oxidation has been extensively studied (ref. 1). The catalysed reaction is important in the clean-up of car-exhaust gases, but a far more demanding situation is to be found within the laser field.

CO₂ TEA lasers, which emit ultra-short pulses of ir radiation in essentially parallel beams, contain a high partial pressure of CO₂ (i.e. 1 atmosphere) some of which during laser operation dissociates



with the result that there is localised arcing. The percentage dissociation of 1 atmosphere CO₂ was shown by Pourbaix in 1948 (ref. 2) to increase with increasing temperature in the manner below.

<u>% decomposition</u>	<u>T(K)</u>
10	2474
1	1841
0.1	1635
0.01	1400
0.001	1225

Originally Pt wire at 1373K was used to catalyse the re-oxidation of the CO produced. On such surfaces not only are oscillations in the rate seen as a result of microfaceting (ref. 3), but also moderate temperatures are required. In other words, the Pt wire was not a particularly good catalyst. More recently Pt/stannic oxide and Pt/Fercalloy have been reported to be more effective in catalysing the recombination of CO and O₂ in sealed CO₂ lasers (ref. 4).

Previously, the oxidation of CO on Pt surfaces has been followed by molecular beam (ref. 5), transient (ref. 6) and theoretical (ref. 7) methods, showing that CO reacts with pre-adsorbed O at 600K rapidly with a first-order collision frequency.

The reverse reaction is very slow and formation of unreactive surface oxygen may be involved. Attention here is given to methods of studying and analysing the activity of Pt-based catalysts in this reaction and to probes which allow rationalisation and interpretation of their surface properties.

EXPERIMENTAL CATALYSTS

Two silica-supported Pt samples were used. (i) 3% Pt/SiO₂ on non-porous Degussa Aerosil 200 was prepared by impregnation to the point of incipient wetness using an aqueous solution of hexachloroplatinic acid (H₂PtCl₆; Johnson Matthey). This was then dried in air at 393K for 16h and reduced in H₂ at 570K. Chemisorption of oxygen suggested that this had a Pt surface area of 31.7 m²/g Pt. (ii) 6.3% Pt/SiO₂ EURO-Pt was used as supplied; its metal area estimated by oxygen chemisorption was 187.7 m²/g Pt and the support exhibited porosity. These catalysts are denoted S3 and S6.

Titania-supported Pt (metal loading 3%) was prepared by impregnation of non-porous Degussa P25 titania, drying and reducing. This is denoted T3.

METHODS

Calorimetry of CO-O Titrations (ref. 8)

A sapphire-calibrated Dupont 990 differential scanning calorimeter (DSC) was used to follow titrations of preadsorbed \underline{O} by CO(g) and preadsorbed \underline{CO} by O₂(g) at constant temperatures on samples (10-25 mg) of the above catalysts. Thermokinetic profiles of heat flow versus titration time were obtained. Reactant gases were 6% CO/N₂ (BOC: 99.995% purity from which traces of oxygen and water had been removed via passage through Pd/alumina and molecular sieve beds) and 12% O₂/N₂ (BOC: 99.995% purity).

Calorimetry of Catalysed CO Oxidation

Previously calorimetry has shown that the rate of heat generation in exothermic reactions is proportional to the rate of catalysed reaction (ref. 9). DSC was used here in CO oxidation with 6% CO/N₂ and 6% O₂/N₂ reactant gases over catalyst samples (20-30 mg) during temperature programming at 10K/min in the range 293-848-293K. Silica was used in the reference pan. A septum was placed at the DSC outlet and from this samples were taken and injected onto a Pye 104 gas chromatograph with a HWD and a silica-gel column at 373K. This separated CO₂ and gave a response which was linear with CO₂ concentration in the relevant range.

Catalysis of CO Oxidation

Studies of the rates of CO oxidation over samples (0.1g) of the catalysts were followed in a micro-reactor with gc-ir analysis of products. Reactant streams of CO/O₂/N₂ were passed at 40 cm³/min through catalyst samples (preheated in flowing N₂ (40 cm³/min) for 30 min at 393K) as these were heated and cooled at 2K/min.

FTIR Microspectroscopy (ref. 10)

Infrared has long been used to probe the nature of CO adsorbed on metal surfaces (ref. 11). The samples were placed in an FTIR cell within an IRPLAN (Spectra-Physics) IR microscope linked to a Perkin Elmer 1710 FTIR through which reactant gases could flow as follows:

- (i) in chemisorption 6% CO/N₂ flowed at 23 cm³/min while heating to 425K at 5K/min before cooling to room temperature
- (ii) in CO oxidation where 6% CO/N₂ (21.4 cm³/min) and 6% O₂/N₂ (21.1 cm³/min) flowed while heating at 425K at 5K/min and holding isothermally for 2h before cooling to room temperature.

RESULTS

Pt/SiO₂

Titration of CO-oxygen at 373K over S6 were entirely repeatable in sustained titration cycles and thermokinetic profiles were identical to those shown in Figure 1, suggesting that the titrations were entirely reversible at this temperature. Interestingly the shapes of the two titrations are different, but it is not yet possible to suggest that the titration with the induction period and lower symmetry is not involving a Langmuir-Hinshelwood mechanism. However, it is tempting to associate the induction period of low heat flux with chemisorption of the gaseous titrant on the preadsorbed monolayer. Interestingly, the induction period on S6 when O_{2(g)} is titrating the CO-covered surface decreases as the temperature of titration rises:

T(K):	293	323	373	423	473	523	573
t(s)	330	168	80	48	0	0	0

At 373K the heat liberated in the two titration steps on S6 is not identical (i.e. 2270J were liberated per g Pt in CO titration of preadsorbed O and 1260J per g Pt were liberated in O₂ titration of preadsorbed CO).

Now consider what calorimetry can reveal about the catalysed CO oxidation reaction. Figure 2 shows that as the temperature of S3 increases, DSC shows a light-off at 473K with a maximum heat flow at 573K of about 75 mJ/s. Bearing in mind the relationship of heat flow and rates of reaction (ref. 9) it might be expected that the catalysed rate would also follow a similar profile. However, this would suggest that the rate of reaction would decrease to a low value at about 773K. This low rate of heat flow is interesting at high temperature and requires further investigation. On decreasing temperature the same type of profile was noted but displaced to a lower temperature than that seen with increasing temperature (i.e. hysteresis is shown). On decreasing temperature oscillations appear close to the point where extinction of the reaction might occur.

Comparison in Figure 3 of DSC-thermokinetic profiles with measured rates during CO oxidation over S3 during temperature programmed analysis confirms the difference between DSC and catalytic analysis especially at highest temperatures of analysis.

There is the suggestion that at these higher temperatures after light-off the reaction does not proceed entirely on the catalyst surface.

Sustained analysis of the catalysis of CO oxidation on S6 (see figure 4) revealed substantial activity-temperature hysteresis loops where activity was stable with reaction time. The hysteresis may in part be aggravated by support porosity (not seen in S3). At high P_{O_2} rates of oxidation are higher than in Figure 3.

Turning now to the micro-FTIR-spectrometry it is seen in Figure 5 that different parts of the top surface of a bed of S6 during CO chemisorption and CO oxidation under isothermal conditions show different spectral characteristics. It is known that average metal surface atom coordination affects the nature of adsorbed CO (ref. 12) and results are consistent with CO on low index crystallographic planes (ref. 13):

- (i) $1890 \pm 9 \text{ cm}^{-1}$ bridge-bound CO
- (ii) $2082 \pm 1 \text{ cm}^{-1}$ linearly-bound CO.

Thus the two areas show little bridge-bound CO in chemisorption, when CO coverage should be almost complete, but a greater proportion of this species during CO oxidation when the CO coverage is lower.

Pt/TiO₂

Results over T3 in Figures 6 and 7 should be compared with those in Figures 1 and 4 for Pt/silica. First, the thermokinetic profiles are different, with much enhanced induction periods and diminished total heat flows. Second, the activity-temperature hysteresis is absent and as expected closer to non-porous S3 than S6. DSC of CO oxidation on 3% Pt/TiO₂ under the same conditions as in Figure 2 showed a light-off at 498K.

DISCUSSION

Isothermal CO-O and O₂-CO titrations have not been widely used on metal surfaces (ref. 14) and may be complicated if some oxide supports are reduced by CO titrant (ref. 15). However, they can illuminate the kinetics of CO oxidation on metal/oxide catalysts (ref. 16) since during such titrations all O and CO coverages are scanned as a function of time. There are clear advantages in following the rates of the catalysed CO oxidation via calorimetry and gc-ms simultaneously. At lower temperatures the evidence they provide is complementary. CO oxidation and its catalysis of CO oxidation have been extensively studied (ref. 1), with hysteresis (ref. 17) and oscillations apparent, and the present results suggest the benefits of a combined approach. Silica support porosity may be important in defining activity-temperature hysteresis.

FTIR microspectroscopy reveals the chemical heterogeneity of the catalytic surfaces used; it is interesting that the evidence with regard to the dominant CO surface species and their reactivities with regard to surface oxygen for present oxide-supported Pt are different from those seen on graphite-supported Pt (ref. 9).

It is clear using these techniques that Pt supported upon reducible oxides behaves differently in this reaction to Pt upon a more unreactive support.

CONCLUSIONS

It is expected that the application of these analytical approaches to this ancient yet intriguing catalytic reaction will lead to a new understanding of the catalytic process and more effective catalysts.

ACKNOWLEDGMENTS

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REFERENCES

1. Engel, T.; and Ertl, G., *Adv. Catal.*, 28, 1979, 1; Gasser, R.P.H., 'Introduction to Chemisorption and Catalysis by Metals', Oxford Univ. Press, 1985.
2. Pourbaix, M.J.N.; and Rorive-Boute, C.M., *Disc. Far. Soc.*, 4, 1948, 141.
3. Schuth, F.; and Wicke, E., *Ber. Bunsen. Phys. Chem.*, 93, 1989, 191; Eiswirth, M.; Moller, P.; and Ertl, G., *Surf. Sci.*, 208, 1989, 13; Tsai, P.K.; Maple, B.M.; and Herz, R.K., *J. Catal.*, 113, 1988, 453; Plath, P.J.; Moller, K.; and Jaeger, N.I., *J. Chem. Soc. Far. Trans. I*, 84, 1988, 1751.
4. Stark, D.S., *Plat. Met. Rev.*, 28, 1984, 166; Stark, D.S.; and Harris, M.R., *J. Phys.*, 21E, 1988, 715.
5. Alnot, M.; Fusy, J.; and Cassuto, A., *Surf. Sci.*, 57, 1976, 651; Pacia, N.; Cassuto, A.; Penetenero, A.; and Weber, B., *J. Catal.*, 41, 1976, 455.
6. Hori, G.K.; and Schmidt, L.D., *J. Catal.*, 38, 1975, 335; White, J.M., *J. Chem. Phys.*, 66, 1977, 5744.
7. Weinberg, W.H.; and Merrill, R.P., *J. Catal.*, 40, 1975, 268.
8. Martin Luengo, M.A.; Sermon, P.A.; and Wurie, A.T., *J. Chem. Soc. Far. Trans. I*, 83, 1987, 1651.
9. Beecroft, T.; Miller, A.W.; and Ross, J.R.H., *J. Catal.*, 40, 1975, 281.
10. Self, V.A.; and Sermon, P.A., *J. Phys. C, Matter* 1, 1989, SB221-SB224.
11. Hollins, P., *Ads. Sci. Tech.*, 2, 1985, 177; Sheppard, N.; and Nguyen, T.T., *Ad. Infrared Raman Spec.*, 5, 1978, 67; Queau, R.; and Poilblanc, R., *J. Catal.*, 27, 1972, 200; Blyholder, G., *J. Phys. Chem.*, 68, 1964, 277.

12. de Koster, A.; Jansen, A.P.J.; van Santen, R.A.; and Geerling, J.J.C., *Far. Disc. Chem. Soc.*, 87, 1989, 221.
13. Crossley, A.; and King, D.A., *Surf. Sci.*, 68, 1977, 528; *Surf. Sci.*, 95, 1980, 131; Bare, S.R.; Hofman, P.; and King, D.A., *Surf. Sci.*, 144, 1984, 347; Eischens, R.P.; and Pliskin, W.A., *Adv. Catal.*, 10, 1958, 1; Blyholder, G., *J. Phys. Chem.*, 68, 1964, 2772.
14. Wentrcek, P.; Kimoto, K.; and Wise, H., *J. Catal.*, 33, 1973, 279; *Langmuir*, I., *J. Amer. Chem. Soc.*, 40, 1918, 1361; Akhtar, M.; and Tompkins, F.C., *Trans. Far. Soc.*, 67, 1971, 2461; Linares-Solano, A.; Rodriguez-Reinoso, F., and Salinas-Martinez de Lecea, C.; *Carbon*, 20, 1982, 177; Falconer, J.L.; Wentrcek, P.R.; and Wise, H., *J. Catal.*, 45, 1976, 248.
15. Pajares, J.A.; Gonzalez de Prado, J.E.; Garcia Fierro, J.L.; Tejuca, L.G.; and Weller, S.W., *J. Catal.*, 44, 1976, 421.
16. Cox, M.P.; Ertl, G.; Imbihl, R.; and Rustig, J., *Surf. Sci.*, 134, 1983, L517.
17. Hlavacek, V.; and Votruba, J., *Adv. Catal.*, 27, 1978, 59.

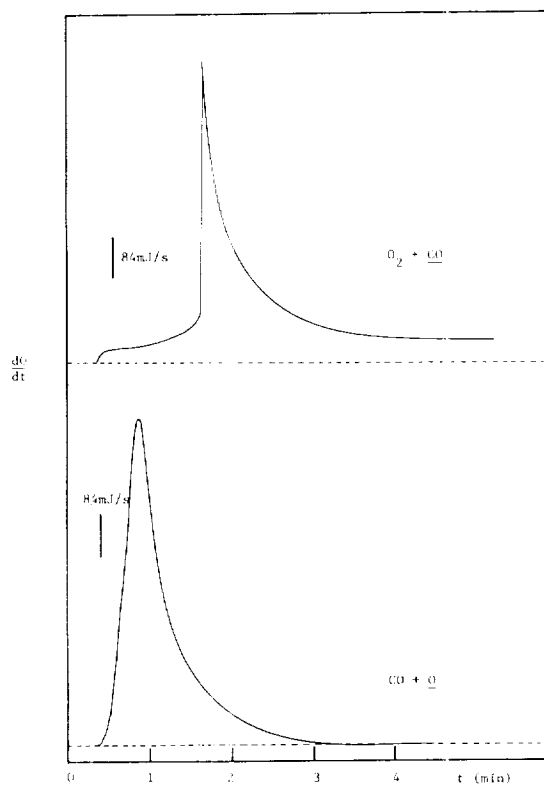


Figure 1 Thermokinetic profiles during titration of pre-adsorbed \underline{O} by $CO(g)$ and preadsorbed \underline{CO} by $O_2(g)$ on Pt/SiO_2 (S6).

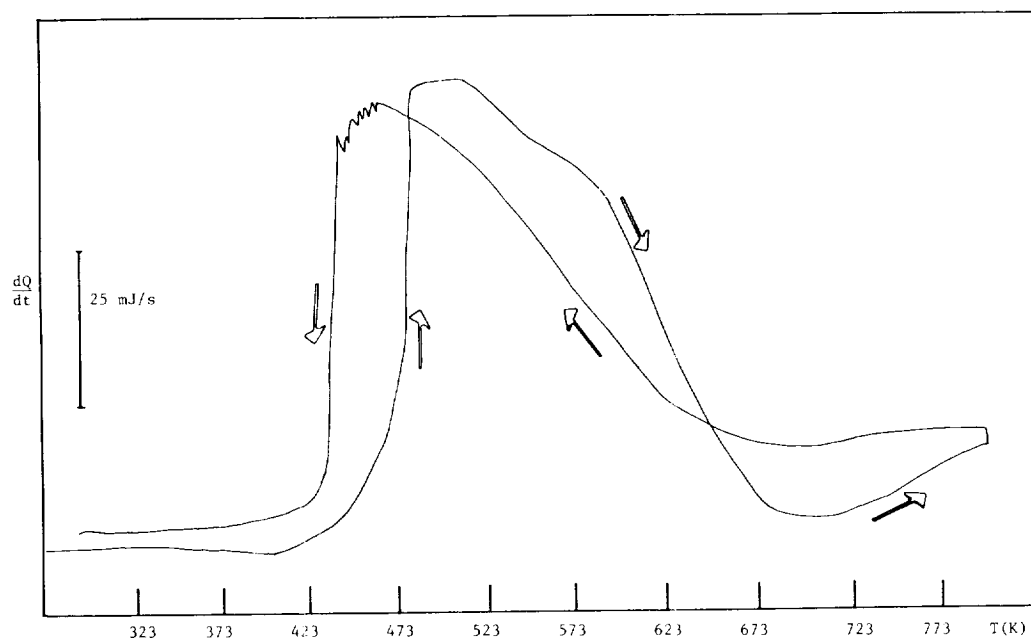


Figure 2 Thermokinetic profiles for CO oxidation ($P_{CO}:P_{O_2}:P_{N_2} = 23:23:714$; $P_{total} = 101 \text{ kPa}$) over $44 \text{ mg } Pt/SiO_2$ during temperature programming at $10K/min$ in the range $328-848-323K$. Oscillations set in at the point at which extinction of the reaction was imminent.

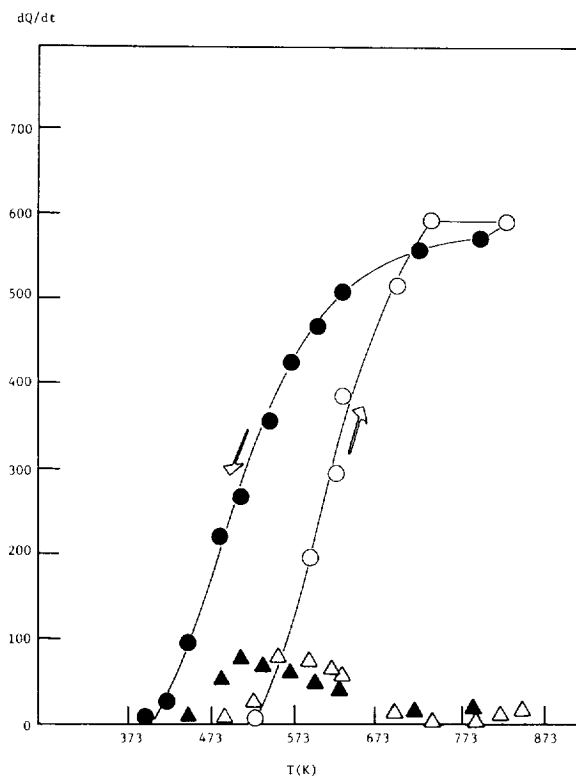


Figure 3 Comparison of thermokinetic (Δ, \blacktriangle) and catalytic (O, \bullet) results for CO oxidation over Pt/SiO_2 during temperature programmed investigation. Conditions as in Figure 3. O, Δ denote increasing temperature and \bullet, \blacktriangle decreasing temperature.

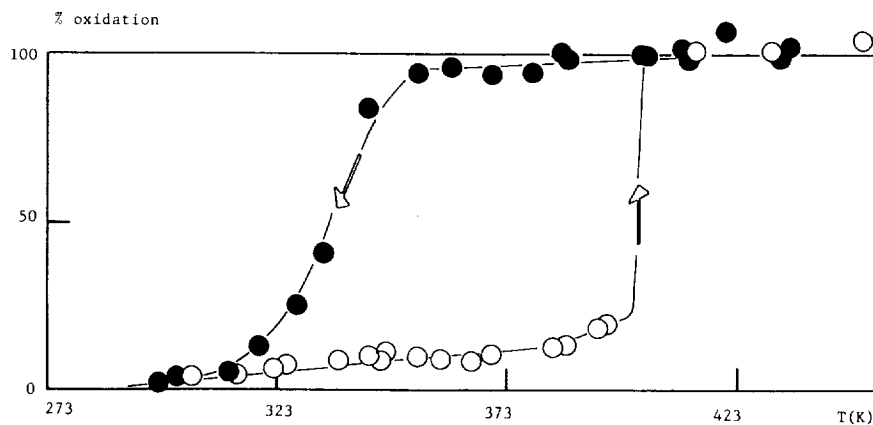


Figure 4 % oxidation of CO (when $P_{CO}:P_{O_2}:P_{N_2} = 15:120:520$; P_{total} is 101 kPa; flow rate $40 \text{ cm}^3/\text{min}$) during programming $273-433-273\text{K}$ at $1\text{K}/\text{min}$ with increasing (O) and decreasing (\bullet) temperature over Pt/SiO_2 . At high temperature there is additional desorption of adsorbed CO_2 . The temperature width of the hysteresis loop at 50% conversion is 60K.

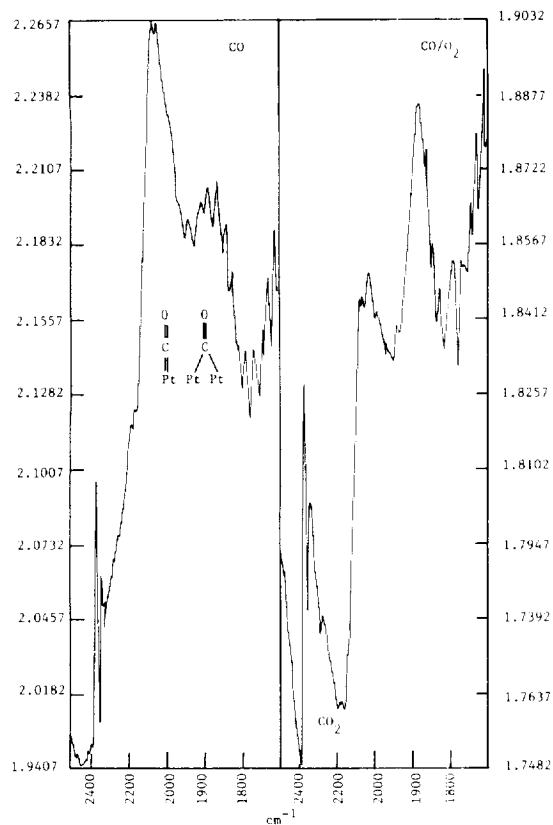


Figure 5

Reflectance FTIR of two areas of the surface of a bed of Pt/SiO_2 during CO chemisorption and CO oxidation.

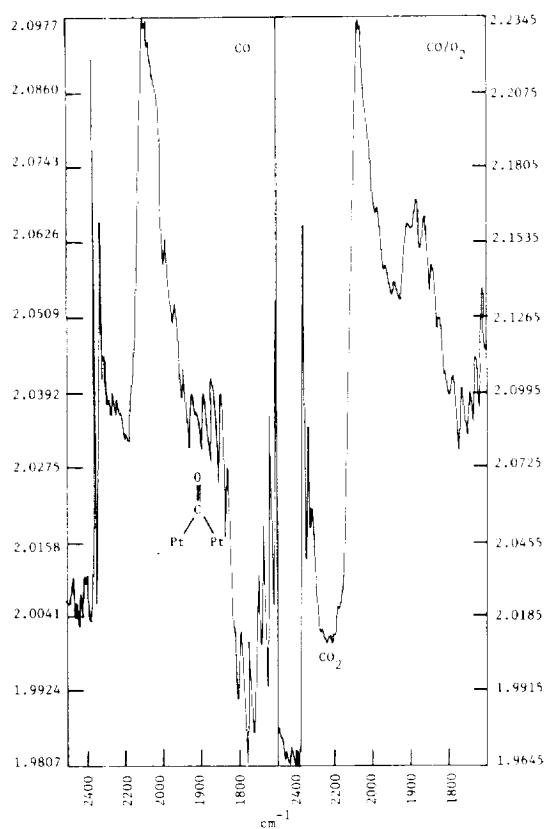


Figure 5 (continued)

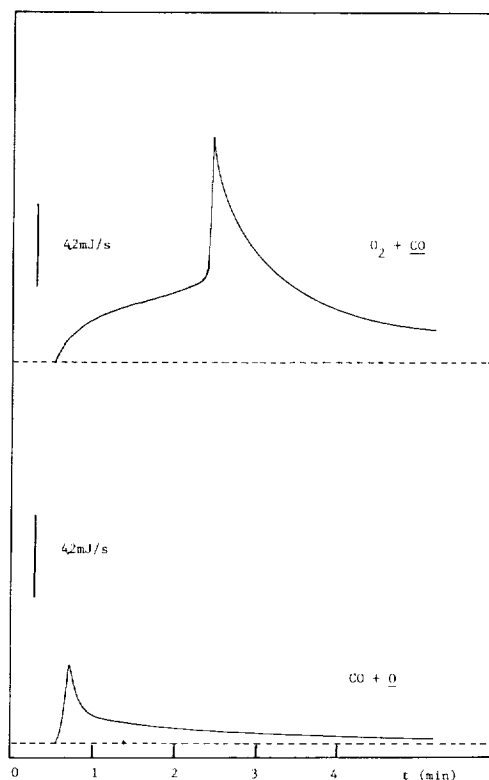


Figure 6 Thermokinetic profiles during titrations of preadsorbed $\underline{\text{O}}$ by $\text{CO}_{(\text{g})}$ and preadsorbed $\underline{\text{CO}}$ by $\text{O}_{2(\text{g})}$ on Pt/TiO_2 . The former shows a greater contribution from the precursor step to that for Pt/SiO_2 (seen in Figure 1).

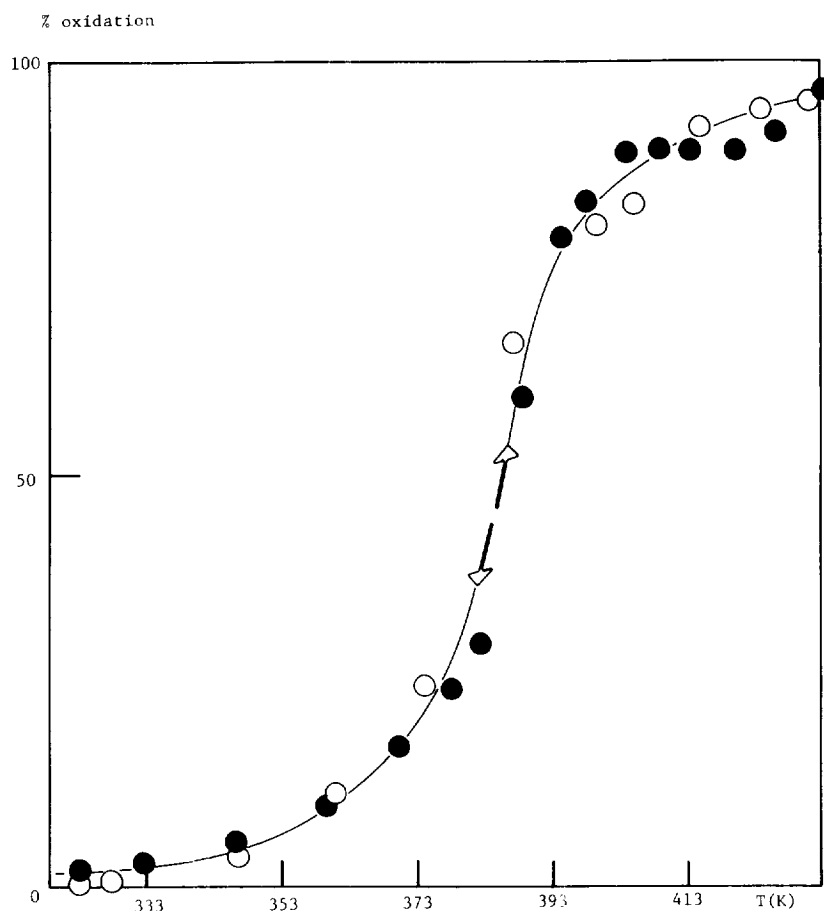


Figure 7 % oxidation of CO under the conditions in Figure 4 over Pt/TiO₂.
 ○ and ● denote data with increasing and decreasing temperature.
 The catalysed reaction occurs at a faster rate at lower temperatures over this catalyst than Pt/SiO₂ (see Figure 4) and without activity-T hysteresis seen when temperatures decreased.

